Photocatalytic Nitrogen Reduction by Ti$_3$C$_2$ MXene Derived Oxygen Vacancy-rich C/TiO$_2$


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Abstract

In this work, oxygen vacancy-rich C/TiO₂ (OV-C/TiO₂) samples were prepared by a one-step calcination approach using Ti₃C₂ MXene as the precursor, and used for the photocatalytic N₂ reduction. The NH₃ yields of all the prepared OV-C/TiO₂ samples exceeded those achieved on commercial anatase TiO₂ and P25, with both H₂O and CH₃OH as the proton sources. Among them, the OV-C/TiO₂-600 offered the remarkable NH₃ synthesis rates, which are 41.00 μmol g⁻¹ h⁻¹ (with H₂O as the proton source) and 84.00 μmol g⁻¹ h⁻¹ (with CH₃OH as the proton sources). The photocurrent and fluorescence spectra showed that OV-C/TiO₂-600 exhibited the highest generation/separation rate and longest lifetime of photocarriers among all the prepared samples. ESR and TPD experiments confirmed much more efficient chemisorption of N₂ on the surface of the prepared OV-C/TiO₂-600 than that on the surface of the commercial anatase TiO₂. Moreover, DFT calculations further demonstrated that N₂ conversion to NH₃ through a Gibbs free energy release leading alternating pathway with a low energy barriers, on the oxygen vacancy on TiO₂ surface.
1. Introduction

Reduction of N\textsubscript{2} to NH\textsubscript{3} is a vital process to promote the growth of the organism.\textsuperscript{1-4} In nature, biological nitrogen fixation and light-driven nitrogen fixation are two main pathways for NH\textsubscript{3} synthesis. However, productions of NH\textsubscript{3} by the two approaches are far away from the agricultural requirements. Hence, artificial nitrogen fixation is a pressing demand for solving the global starvation problem.\textsuperscript{5} More than a century ago, German chemist Fritz Haber contrived Haber-Bosch process to manufacture NH\textsubscript{3} by N\textsubscript{2} and H\textsubscript{2} at drastically high temperature (> 673 K) and pressure (> 200 bar).\textsuperscript{6-10} About a decade ago, Greek chemists Marnellos and Stoukides synthesized NH\textsubscript{3} using H\textsubscript{2} and N\textsubscript{2} diluted by He in an electrolytic cell with the solid electrolyte of strontium-cerium-yttrium-perovskite porous ceramics at 843 K and atmospheric pressure, improving NH\textsubscript{3} yield from 15% (Haber-Bosch process) to 78%.\textsuperscript{11} Notably, the reaction conditions of the two methods are still very harsh with intensive energy consumption and environmental pollution.\textsuperscript{12} Thus a safe, clean and sustainable NH\textsubscript{3} synthesis processes are urgently demanded.\textsuperscript{13}

Semiconductor photocatalysis as a clean and sustainable technology has been applied in many fields, such as water splitting, pollutant elimination, CO\textsubscript{2} reduction, CH\textsubscript{4} activation, as well as N\textsubscript{2} fixation.\textsuperscript{14} As early as in 1977, Schrauzer and Guth reported the groundbreaking research on photolysis of N\textsubscript{2} to NH\textsubscript{3} on TiO\textsubscript{2}.\textsuperscript{15} Since then, the photocatalytic N\textsubscript{2} fixation becomes highly attractive as a promising strategy for NH\textsubscript{3} synthesis under mild conditions.\textsuperscript{16-22} However, its development is barely satisfactory for the long term in the following decades.\textsuperscript{23} This is due to the difficulty of breaking the highly stable N≡N triple bond, whose bond energy is as high as 941 kJ/mol.\textsuperscript{4} This is still an enormous challenge for all scientists today. Until recently, some prospective semiconductors, TiO\textsubscript{2},\textsuperscript{4, 12, 15, 24-32} SrTiO\textsubscript{3},\textsuperscript{33} BaTiO\textsubscript{3},\textsuperscript{34} CdS,\textsuperscript{6} BiOX,\textsuperscript{1, 23, 35-37} g-C\textsubscript{3}N\textsubscript{4},\textsuperscript{38-41} and WO\textsubscript{3},\textsuperscript{42, 43} have been successively used for photocatalytic N\textsubscript{2} fixation. Among them, TiO\textsubscript{2}-based semiconductors are the most stable and robust photocatalysts, but they still suffer from low efficiency. Notably, oxygen vacancies on the surface of TiO\textsubscript{2}\textsuperscript{4, 12} and BiOBr\textsuperscript{1, 23} have been proved to be effective for photocatalytic N\textsubscript{2} fixation, due to their favorable adsorption of N\textsubscript{2} molecules and high reduction potential of conduction band electrons. Hence, constructing oxygen vacancies on the surface of semiconductors is a promising strategy to improve the photocatalytic efficiency of N\textsubscript{2} fixation.
Scheme 1 Diagram of the preparation process of OV-C/TiO$_2$.

Ti$_3$C$_2$ MXene is a new layered material without noble metal, which was firstly synthesized in 2011$^{44}$ and has been widely applied as co-catalysts in photocatalysis$^{45-51}$. Meanwhile, it is also a good TiO$_2$ precursor, from which abundance of vacancies can be created.$^{52-53}$ Herein, OV-C/TiO$_2$ samples were prepared through one calcination step by using Ti$_3$C$_2$ MXene as the precursor (Scheme 1), which was synthesized by etching Al layers from the Ti$_3$AlC$_2$ in HF at room temperature$^{54}$. Abundance of oxygen vacancies and C doping was observed in the as-prepared TiO$_2$ sample. Hence, this OV-C/TiO$_2$ was prospected to have a high ability to convert N$_2$ to NH$_3$ under sunlight irradiation. The experimental results in this work showed that, over all the prepared OV-C/TiO$_2$ samples under full spectrum light irradiation, NH$_3$ was successfully generated from N$_2$ with either H$_2$O and CH$_3$OH as the proton source. Remarkably, the efficiency of N$_2$ fixation was achieved at the OV-C/TiO$_2$-600 sample. All the data of NH$_3$ yields were detected by ion chromatography method to prove the effectiveness of the photocatalyst.$^{55}$ The origin of the N source of the produced NH$_3$ was studied by the isotope labeled N$_2$ ($^{15}$N$_2$ and $^{14}$N$_2$), the different products were identified by $^1$H spectra of nuclear magnetic resonance (NMR). This excellent N$_2$ fixation was proposed due to high generation/separation rate of photocarriers with prolonged lifetime, the efficient N$_2$ adsorption on the abundance of oxygen vacancies, as well as the low-energy-barrier pathway of N$_2$ to NH$_3$ on oxygen vacancy. The mechanism of high photocatalytic activity for NH$_3$ synthesis over OV-C/TiO$_2$ we prepared were further discussed based on the measurements of photoelectrochemical experiments, fluorescence spectra, electron...
2. Experimental Section

2.1. Materials

Ti$_3$AlC$_2$ MAX phase powders (>98 wt% purity) were purchased from Laizhou Kaixi Ceramic Materials Co., Ltd. (Shandong, China). Ethanol (AR) and hydrofluoric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Ammonium chloride and sodium hydroxide and sodium were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Ultrapure water (18.2 MΩ cm) used throughout all experiment was purified through Millipore Milli-Q system. All chemical reagents were used as received without further purification.

2.2. Preparation of OV-C/TiO$_2$

Ti$_3$C$_2$ MXene was synthesized by HF-etching method according to the reported literature.$^{54}$ In detail, 1 g of Ti$_3$AlC$_2$ was added into 20 mL 40% HF solution with magnetic stirring at room temperature for 24 hours. The resulting product was washed with deionized water and ethanol several times until pH > 6. The precipitates were sonicated with the dispersion of water for 1 hour and then centrifuged at 3500 rpm for 1 hour to obtain Ti$_3$C$_2$ MXene. To prepare OV-C/TiO$_2$, the prepared Ti$_3$C$_2$ MXene was heated to different temperatures (400, 500, 600, 700 and 800℃, respectively) in air at a rate of 5℃/min and kept for 2 hours. The resultant samples were denoted as OV-C/TiO$_2$-X, herein X represents the annealing temperature, being 400, 500, 600, 700 and 800, respectively.

2.3. Characterizations

The SEM images were collected from Hitachi SU-8010 scanning electron microscopy with an operating voltage of 5 kV. The TEM and HRTEM images were performed using an FEI Tecnai G2 F20 transmission electron microscope operated at 200 kV. The specific surface areas were determined using a surface analyzer (Tristar II3020) through nitrogen adsorption and desorption isotherms at 77 K by Brunauer-Emmett-Teller (BET) method. The XRD patterns were recorded on a Bruker AXS-D8 diffractometer using Cu Kα radiation. The UV-vis DRS spectra were recorded
by UV-vis spectrophotometer (U-3310, HITACHI) equipped with a diffuse reflectance accessory, using BaSO$_4$ as the reflectance standard reference. The low temperature ESR spectra were recorded on a Bruker EXM EPR Spectrometer at 77 K. The XPS experiments were carried out by PHI 5000 VersaProbe II XPS system. All binding energies were referenced with respect to the C1s peak (284.6 eV) of the surface adventitious carbon. The photoluminescence spectra decay curves were obtained by using FLsp920 with EPL375 as the light source. The adsorptions of N$_2$ on the surface of the commercial TiO$_2$ and prepared OV-C/TiO$_2$-600 were performed on a TPD equipment (Maike, Autochem II 2920, TCD detector). Specifically, 100 mg sample was pretreated at 300 °C for 2 hours, and then heated to 450 °C at a rate of 10 °C/min with a gas flow rate of 50 mL/min, and kept for two hours.

2.4. Electrochemical tests

The Transient photocurrent responses was performed on a Princeton 283 electrochemical workstation equipped with a standard three-electrode cell with 1M Na$_2$SO$_4$ as the electrolyte and a Xe-lamp (HSX-F/UV 300) as the light source. An ITO glass electrode (20×30×0.4mm, 7-10 Ω) coated with photocatalyst (drop coating), a platinum foil and a saturated calomel electrode were employed as the working electrode, the counter electrode and the reference electrode respectively. EIS test was performed on CHI 660E electrochemistry workstation (Chenhua Instrument) with a standard three-electrode cell system. The working electrode was a glassy carbon electrode (d = 3 mm, S = 0.0707 cm$^2$), the counter electrode was a platinum foil and the reference electrode was a saturated calomel electrode. For preparing working electrode, 5 mg of powder and 0.1 mL of Nafion solution (5 wt %) were dispersed in 0.9 mL absolute ethanol to form a homogeneous ink, and 4 μL ink was loaded onto glassy carbon electrode via drop coating technique. Electrochemical impedance spectra (EIS) were conducted in the frequency range of 1 mHz to 100 kHz under relatively open circuit voltage, using 0.5 M NaSO$_4$ solution as electrolyte. The EIS spectra were collected both under light irradiation and in the dark.

2.5. Photocatalytic nitrogen reduction

The photocatalytic N$_2$ reduction experiments were carried out in N$_2$ atmosphere at room temperature using a 300 W Xe lamp (PLS-SXE300D, 200-800 nm) as the light source, with either
H₂O or CH₃OH as the proton source. Typically, 50 mg of catalyst was dispersed in 50 mL of ultrapure water and then transferred to the reactor equipped with water circulation in the outer jacket in order to maintain at the temperature of 25 °C. The methanol concentrations in the system are 0.01 M, when using methanol as the proton source. Before irradiation, the mixture was continuously stirred in the dark with pure N₂ (99.999%) bubbling at a flow rate of 50 ml min⁻¹ for 30 minutes and then irradiated for 120 minutes. During the period of a photocatalytic reaction, 1 mL of the solution was sampled every 30 minutes for product analysis. The ammonia concentration was detected by ion chromatography (IC, SHINE CIC-D120) equipped with an Ionpac CS16 column (4 × 250 mm, Dionex), a suppressor (SHY-A/C), and a conductivity detector. The eluent was 30 mM CH₃O⁻S solution, the flow rate was 0.5 mL/min, and the suppress current was 50 mA. Notably, ion chromatography (IC) method is much more reliable than Nessler or indophenol blue (IB) method. Before catalysts were removed by filtration, 500 μL 0.1 M HCl solution was added to 500 μL suspension for 5 minutes. Consequently, the obtained solutions were diluted by 4 mL ultrapure water for measurement. The retention time of NH₄⁺ is at about the 11th minute. Absolute calibration of the method was done using ammonium chloride solutions of known concentration as standards.

The photocatalytic generations of ·OH over OV-C/TiO₂-600 sample was measured by a fluorescence method using coumarin as a chemical trap. The photocatalysts were dispersed in a 30ml aqueous solution of 1 mM coumarin, and stirred for 30 min in the dark before UV-vis light irradiation. 3 ml suspension was sampled and separated by centrifugation at a given irradiation time interval (5 min). The fluorescence emission intensity evolution of 7-hydroxycomumarin (7-HC), a highly fluorescent product formed by the coumarin and ·OH, was detected at about 450 nm under the excitation at 350 nm using a spectrofluorometer (PerkinElmer LS55).

\[
\begin{align*}
\text{(coumarin)} + \cdot \text{OH} & \rightarrow \text{(7-hydroxycomumarin)} \\
\end{align*}
\]

The production of the liquid product HCHO was measured by colorimetry. Specifically, 15 g of ammonium acetate, 0.3 mL of acetic acid, and 0.2 mL of pentane-2,4-dione were dissolved in
water to prepare 100 ml of a color reagent aqueous solution. After diluting 0.5 ml of the test solution with 2 ml of water, mixed it with 0.5 ml of the chromogenic reagent aqueous solution and maintained at room temperature for 1 hour. The absorbance at 412 nm was measured by UV-Vis absorption spectroscopy.

The apparent quantum yields (AQY) were determined using monochromatic filter of 400 nm and 420 nm with a bandwidth of 5 nm, to carried out the photocatalytic N\textsubscript{2} reduction. The calculated as follows:\textsuperscript{12}

\[
\text{AQY} = 100\% \times \left(\frac{3 \times \text{generated ammonia molecular number}}{\text{incident photon number}}\right)
\]

2.6. \textsuperscript{15}N\textsubscript{2} isotope Labeling Experiments \textsuperscript{58}

An isotope labeling experiments were carried out to clarify the N source of generated NH\textsubscript{3}, by using \textsuperscript{14}N\textsubscript{2} and \textsuperscript{15}N\textsubscript{2} as the feeding gas. The \textsuperscript{14}NH\textsubscript{3} and \textsuperscript{15}NH\textsubscript{3} were distinguished by NMR spectra of \textsuperscript{1}H of NH\textsubscript{4}\textsuperscript{+}. As displayed in Figure S1, the NMR peak of \textsuperscript{1}H is divided into triple peaks by \textsuperscript{14}N and and double peaks by \textsuperscript{15}N isotopes, for standard \textsuperscript{14}NH\textsubscript{4}Cl and \textsuperscript{15}NH\textsubscript{4}Cl. The number of peaks (N) in accordance with the theory calculations: \(N = 2nI + 1\). This formula means that the NMR peak of \textsuperscript{1}H will be divided to several peaks due to N isotopes, where \(n\) represents the number of N atoms, and \(I\) is the spin quantum number of isotope N: \(I = 1\) for \textsuperscript{14}N and \(I = 1/2\) for \textsuperscript{15}N. In addition, from Figure S1, the coupling constant of the triple peaks is 52.3 Hz for \textsuperscript{14}NH\textsubscript{4}Cl, while the coupling constant of double peaks is 73.2 Hz for \textsuperscript{15}NH\textsubscript{4}Cl.

After the photocatalytic NH\textsubscript{3} synthesis by OV-C/TiO\textsubscript{2}-600 for 2 hours, the obtained \textsuperscript{14}NH\textsubscript{3} and \textsuperscript{15}NH\textsubscript{3} were distinguished by \textsuperscript{1}H nuclear magnetic resonance (NMR, 400 MHz). The typical NMR signals of \textsuperscript{1}H for \textsuperscript{14}NH\textsubscript{4}\textsuperscript{+} and \textsuperscript{15}NH\textsubscript{4}\textsuperscript{+} were detected using \textsuperscript{14}N\textsubscript{2} and \textsuperscript{15}N\textsubscript{2} as the feeding gas. In this process, the prepared NH\textsubscript{3} solutions were concentrated by distillation before being added to deuterated DMSO.

2.7. DFT calculations

The spin-polarized projector augmented wave (PAW) pseudopotentials via the Vienna Ab initio Simulation Program (VASP) were used to perform the density functional theory (DFT) calculations.\textsuperscript{59-62} The exchange and correlation energy were described by the generalized gradient
approximation (GGA) via Perdew-Burke-Ernzerhof (PBE) functional. The constituted atomic valence states adopted were H 1s², N 2s²2p³, O 2s²2p⁴, and Ti 3p⁶3d³4s¹. The plane wave cut-off energy was 450 eV and a 7×7×3 grid of Monkhorst-Pack points were employed for geometry optimization of a 12-atom conventional cell of anatase TiO₂. Geometry optimizations were obtained by minimizing the total energy using a quasi-Newton algorithm to relax ions until it converged within 10⁻⁴ eV and the forces on each ion were less than 0.05 eV/Å. During the geometry optimization, volume and shape of the cell as well as atomic positions were relaxed.

For the anatase (1 0 1) surface with an oxygen vacancy (S₀v), a vacuum region of at least 15 Å was used, so that the slabs in neighbouring cells in the vertical direction are separated by a sufficiently large distance. During the geometry optimization, the first three O-Ti-O-layers of the atoms were allowed to relax until reaching a 10⁻⁴ eV convergence in the total energy, while the forces on each ion were less than 0.05 eV/Å with the three remaining O-Ti-O-layers being kept fixed (bulk like). To avoid the interaction among adsorbed molecules in neighboring cells, supercells with 10.3×15.2 Å units of surfaces are constructed. To investigate the mechanisms of N₂ reduction on the oxygen vacancy on TiO₂ surface, we carried out the DFT-D3 method with Becke-Jonson damping. We studied the most plausible N₂ adsorption configuration on the S₀v. The structure after the geometric relaxation is shown in Figure S2, which was drawn using the VESTA software.

The adsorption energy (Eₐdₖ) was calculated using the equation:

\[ ΔE = E_{adₖ} = E_{gas@S₀v} - E_{S₀v} - E_{gas} \]  

In Eq. 1, ΔE is the reaction energy, E_{S₀v} is the total energy of the anatase (1 0 1) surface with an oxygen vacancy, E_{gas@S₀v} is the total energy of E_{S₀v} with gas adsorbed, and E_{gas} is the total energy of the isolated species (N₂, NH₃, H⁺+e⁻). In the present models, the chemical potential of a proton-electron pair, μ (H⁺)+μ (e⁻), was equal to the half of the chemical potential of one gaseous hydrogen, 1/2 μ (H₂).

In all fundamental reaction steps, reaction Gibbs free energy changes were calculated using formula:

\[ ΔG = ΔE + ΔZPE - TΔS \]  

In Eq. 2, ΔZPE is the difference to zero point energies due to the reaction, and ΔS is the entropy.
change, respectively. Because the temperature $T = 0$ K was used in the $\Delta G$ calculation of each reaction step, Eq (1) can be written as:

$$\Delta G = \Delta E + \Delta ZPE$$  \hspace{1cm} (3),

meaning $\Delta G$ are corrected via computing the vibrational frequencies of surface species for the $\Delta ZPE$.

3. Results and Discussions

3.1. Characterizations

![Figure 1](image)

**Figure 1** (A) SEM image of Ti$_3$C$_2$ MXene, (B) and (C) SEM images of OV-C/TiO$_2$-600, (D) HRTEM image of OV-C/TiO$_2$-600.

The micromorphology and architectural structures of Ti$_3$C$_2$ MXene and the calcined OV-C/TiO$_2$ samples were characterized by scanning electron microscopy (SEM). In Figure 1A, the layered structure of Ti$_3$C$_2$ MXene is clearly observed, which comes from etching the Al layers of Ti$_3$AlC$_2$ MAX phase.$^{52,53}$ After the oxidation at high temperature in air, its layered structure remained (Figure 1B and S3-6). Meanwhile, type II adsorption isotherms in Figure S7 also suggest multilayer structures of Ti$_3$C$_2$ MXene and as-prepared samples.$^{71}$ The surface areas of all the prepared samples were also evaluated by Brunauer-Emmett-Teller method and listed in Table S1.
All samples show relatively small surface areas, while OV-C/TiO$_2$-600 has the largest of 16.9 m$^2$ g$^{-1}$. As shown in Figure 1C, large amounts of small crystal particles (100 nm - 300 nm) with regular octahedral structure were formed along with the layers. The crystal structure of the particles was further identified by high-resolution transmission electron microscopy (HRTEM) in Figure 1D. Two sets of intersectant fringes with the lattice spacing of 0.231 nm and 0.235 nm can be indexed to (112) and (004) planes of anatase TiO$_2$, while no crystal lattice of Ti$_3$C$_2$ MXene was found.$^{52}$

**Figure 2** (A) XRD full spectra, (B) Raman spectra (inset: Raman spectra of OV-C/TiO$_2$-400), (C) UV-vis DRS spectra, (D) ESR spectra of OV-C/TiO$_2$ derived by Ti$_3$C$_2$ MXenes calcined at different temperatures.

The crystal structures of calcined samples were further confirmed by X-ray diffractometer spectra. The XRD patterns described in Figure 2A show good tetragonal crystal phase of anatase TiO$_2$, all the peaks are in accordance with the standard database (JCPDS No. 21-1272) of anatase TiO$_2$, while no (002) peak of Ti$_3$C$_2$ MXene crystal appears at 9°-10°.$^{52}$ The crystal lattice parameters of OV-C/TiO$_2$-600 calculated by Jade 5 are listed in Table S2, which is consistent with the results of HRTEM in Figure 1D. Raman spectra (Figure 2B) was also obtained to confirm the
conversion of Ti$_3$C$_2$ MXene to TiO$_2$. The four sharp peaks below 750 cm$^{-1}$ for all the samples are attributed to the band modes of TiO$_2$,$^{45, 52}$ while the wide peak at the range of 1000 - 2000 cm$^{-1}$ for the sample of OV-C/TiO$_2$-400 (inset of Figure 2B) were attributed to the residual of Ti$_3$C$_2$ MXene.$^{45}$ However, the peaks derived from residual Ti$_3$C$_2$ MXene disappeared when the calcination temperature is higher than 500°C, suggesting the absolute conversion of Ti$_3$C$_2$ MXene to TiO$_2$. Meanwhile, no peaks at 1350 cm$^{-1}$ and 1590 cm$^{-1}$ related to amorphous carbon$^{52}$ are observed in the Raman spectra of all the samples prepared at the temperature higher than 400 °C. More detailed observation in Figure S8 indicates that (101) diffraction peaks of the prepared OV-C/TiO$_2$ samples significantly shift to higher 2θ values compared with the standard data, but no regulation with the increase of the calcination temperature. According to Bragg’s law, the high 2θ value of the diffraction peaks means shrinkage of the crystal lattice, while the low 2θ value means an expansion of the crystal lattice.$^{71}$ Therefore, C doping was proposed, which could cause the 2θ angle shifts to smaller value, but be offset by oxygen vacancies.$^{55}$ The unclear trend was thus believed due to the cooperative effects of the oxygen vacancies introduction and C doping.$^{12, 74}$

The introduction of oxygen vacancies can also be proved by UV-vis diffuse reflectance (UV-vis DRS) and electron spin-resonance spectroscopy (ESR). As displayed in Figure 2C, all samples exhibit an extended absorption in the range of 400 - 700 nm with a threshold at about 400 nm. The absorption threshold at about 400 nm can be corresponding to the intrinsic band gaps absorption of TiO$_2$, while the wide absorption in the range of 400 - 700 nm is attributed to the introduction of oxygen vacancies.$^{76}$ Its lowering trend suggest the decrease of the oxygen vacancy concentration with the increase of calcination temperature.$^{76}$ In addition, electron spin resonance (ESR) was also used to characterize the existence of oxygen vacancies in the prepared TiO$_2$ samples. Herein, distinctive responses near g value of 2.003 in Figure 2D is related to the typical signals of the unpaired electrons of oxygen vacancies,$^{77}$ which shows a decreased trend with the increase of calcination temperature. These results again suggest the decreased oxygen vacancies of OV-C/TiO$_2$ samples with the increase of calcination temperature, being consistent with the UV-vis DRS results. In brief, fewer oxygen vacancies were formed in the structure of TiO$_2$ at higher temperatures.
Figure 3 High-resolution XPS spectra of C1s (A), O1s (B) and Ti2p (C) spectra of OV-C/TiO$_2$-600.

X-ray photoelectron spectroscopy was conducted to investigate the chemical compositions and oxygen vacancies of the prepared OV-C/TiO$_2$-600 sample. The XPS survey spectra in Figure S9 reveal the presence of Ti, O and C in the sample of OV-C/TiO$_2$-600. Then, the high resolution XPS spectra of C 1s, O 1s and Ti 2p are shown in Figure 3A - C, respectively. The C 1s peak in Figure 3A can be divided into 4 peaks at 287.1 eV, 285.9 eV, 284.6 eV, and 283.9 eV, indicating the carbon of C=O, C-C, C=C and C-Ti species. Four types of oxygen are observed in Figure 3B, and the peaks at 533.3 eV, 531.9 eV, 530.5 eV and 529.1 eV are assigned to adsorption oxygen groups, oxygen near oxygen vacancy, Ti-O-H oxygen and Ti-O-Ti oxygen, respectively. In Figure 3C, two peaks located at 465.1 eV and 459.2 eV are ascribed to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ of typical Ti-O bond in TiO$_2$, while the peaks at 463.7 eV and 457.9 eV are attributed to Ti-C bond, confirming the doping of carbon in TiO$_2$. Meanwhile, Ti$^{III}$ vacancy peaks at 463.3 eV and 457.4 eV are also observed, further suggesting the formation of oxygen vacancy. The oxygen vacancies could be formed on the interface between Ti$_3$C$_2$ MXene and TiO$_2$ when C in the crystal of Ti$_3$C$_2$ reacted with the closest O in the crystal of TiO$_2$, releasing CO$_2$.

Based on the results and discussions, the samples we obtained by Ti$_3$C$_2$ MXene oxidation at different temperatures are OV-C/TiO$_2$ nanoparticles, which can distinctly indicate the structure of the prepared catalyst.

3.2. Photocatalytic fixation of N$_2$

The prepared OV-C/TiO$_2$ samples in this work show excellent performances for photocatalytic NH$_3$ synthesis with both H$_2$O and CH$_3$OH as the proton sources. As shown in Figure 4A, all the prepared OV-C/TiO$_2$ photocatalysts exhibited higher activity for ammonia
production than the commercial anatase-TiO\textsubscript{2} (0 \, \mu\text{mol g}^{-1} \, \text{h}^{-1}) and P25 (1.55 \, \mu\text{mol g}^{-1} \, \text{h}^{-1}), when we used H\textsubscript{2}O as the proton source. Among them, OV-C/TiO\textsubscript{2}-600 generated the most NH\textsubscript{3} with the rate of 41 \, \mu\text{mol g}^{-1} \, \text{h}^{-1}, although it has 3 times smaller surface area (16.9 m\textsuperscript{2} g\textsuperscript{-1}) than the referred P25 TiO\textsubscript{2} (50.0 m\textsuperscript{2} g\textsuperscript{-1}). However, it is difficult to detect the production of O\textsubscript{2}, the product of hole oxidation with H\textsubscript{2}O, which may be due to its over low production. Therefore, we tested the production of \cdot\text{OH} formed by the valence hole oxidation under visible light irradiation, with the coumarin method (Figure S10). Further, we used CH\textsubscript{3}OH to replace H\textsubscript{2}O as the proton source, the photocatalytic production of NH\textsubscript{3} over all the sample were significantly improved (Figure 4B), and the highest NH\textsubscript{3} production was achieved to 84 \, \mu\text{mol g}^{-1} \, \text{h}^{-1} at OV-V/TiO\textsubscript{2}-600. Meanwhile, the generation of HCHO in this system, which was produced by the oxidation of CH\textsubscript{3}OH by the valence hole, was also detected by UV-vis absorbance spectra (Figure S11). In addition, the control experiments by commercial anatase TiO\textsubscript{2} particle were also carried out for a comparison.

The results in Figure 4C and D further confirm that OV-C/TiO\textsubscript{2}-600 photocatalyst is active for photocatalytic N\textsubscript{2} fixation, and negligible NH\textsubscript{3} was observed in the absence of either full spectrum light or N\textsubscript{2}. These results indicate that OV-C/TiO\textsubscript{2} is necessary for catalytic synthesis of NH\textsubscript{3}, as well as the light irradiation. The prepared OV-C/TiO\textsubscript{2} samples in this work show a comparable NH\textsubscript{3} production rate compare to the other TiO\textsubscript{2}-based photocatalysts over the past 5 years (Table S3). This outstanding N\textsubscript{2} fixation performance of OV-C/TiO\textsubscript{2} reveals the critical role of vacancies introduction. It is worth to note that the concentration of oxygen vacancy and C doping in photocatalysts is very important to their photocatalytic activity. As most of the heteroatom doping, oxygen vacancy and C introduction acts not only as the separation center of photogenerated carriers, but also as the recombination center of photogenerated carriers. Therefore, both too much or over low vacancies can not enhance the photocatalytic activity of photocatalyst. This is the main reason for the highest photocatalytic activity was achieved on OV-C/TiO\textsubscript{2}-600. In addition, NH\textsubscript{3} generation yields almost remained steady over four photocatalytic cycling experiments, indicating the good stability of OV-C/TiO\textsubscript{2}-600 sample (Figure 4E and F). The apparent quantum yields (AQY) of the photocatalytic N\textsubscript{2} reduction over the prepared OV-C/TiO\textsubscript{2}-600 were also measured under the homogeneous light, with H\textsubscript{2}O as the proton source. They are 0.04\% for the light of 400 nm and 0.01\% for the light of 420 nm, respectively (Figure S12).
Figure 4 (A) NH₃ generation on OV-C/TiO₂ under UV-vis illumination for 2 hours with H₂O as the proton source, (B) NH₃ generation on OV-C/TiO₂ under UV-vis illumination for 2 hours with CH₃OH as the proton source, (C) Control experiments of NH₃ generations for OV-C/TiO₂-600 with H₂O as the proton source, (D) Control experiments of NH₃ generations for OV-C/TiO₂-600 with CH₃OH as the proton source, (E) Cycling experiments of NH₃ synthesis in 2 hours on OV-C/TiO₂-600, with H₂O as the proton source, (F) Cycling experiments of NH₃ synthesis in 2 hours on OV-C/TiO₂-600, with CH₃OH as the proton source.

Isotope labeling experiments were conducted to confirm that the N source of the produced NH₃. According to the previous report,²⁸ the experimental results by OV-C/TiO₂-600 using ¹⁴N₂
and $^{15}$N$_2$ as the feeding gas are clearly shown in Figure 5. Being consisted with the standard data in Figure S1, the isotope labeling experimental results support that the produced NH$_3$ is generated from the direct photo-reduction of N$_2$ over OV-C/TiO$_2$.

![Figure 5](image)

**Figure 5** $^1$H NMR spectra of $^{15}$NH$_4^+$ and $^{14}$NH$_4^+$ ions produced by OV-C/TiO$_2$ using $^{15}$N$_2$ and $^{14}$N$_2$ as the feeding gas.

### 3.3. Mechanism

In order to further understand the underlying mechanism on the high photocatalytic N$_2$ fixation performance over OV-C/TiO$_2$-600, some more experiments were carried out. Firstly, photocurrent densities were measured to investigate the generations of electron-hole pairs. As displayed in Figure 6A, the photocurrent density of OV-C/TiO$_2$-600 is slightly larger than those of other samples, suggesting the highest charge generation rate.$^1$ Secondly, electrochemical impedance spectra both under the light irradiation (Figure 6B) and in the dark (Figure S13) were also performed to study the charge migration of the prepared OV-C/TiO$_2$ samples. Smaller diameter of the semi-circle in a Nyquist plot means a smaller charge-transfer resistance for a photocatalyst.$^{12}$ The OV-C/TiO$_2$-600 shows the significantly smallest diameters among all the samples both with and without light irradiation, indicating the smallest charge-transfer resistance. Meanwhile, the charge resistances under light irradiation of all the samples are smaller than those in the dark, which may be caused by the electron excitation. Lastly, the lifetime data of the
Photocarriers collected from the time-resolved photoluminescence spectra (Table S4) show that OV-C/TiO₂-600 has the longest average decay time (5.58 ns) compared with other samples (commercial TiO₂: 4.80 ns; OV-C/TiO₂-400: 2.88 ns; OV-C/TiO₂-500: 3.35 ns; OV-C/TiO₂-700: 5.44 ns; OV-C/TiO₂-800: 4.08 ns). Longer decay time implies a longer lifetime of the photogenerated charge carriers. The high generation rate, efficient charge migration and long lifetime of photogenerated electron-hole pairs on OV-C/TiO₂-600 are considered to be the main reasons of the highest photocatalytic activity for N₂ fixation, which was caused by the abundance of oxygen vacancies and carbon doping of the sample. However, oxygen vacancies and doped C can not only act as the separation center, but also work as the recombination center of the photogenerated electron-hole pairs.

OV-C/TiO₂-600 shows the biggest photocurrent density and longest decay time.

**Figure 6** (A) Photocurrent responses of OV-C/TiO₂ derived by Ti₃C₂ MXene calcined at different temperatures, (B) Electrochemical impedance spectra Nyquist plots of OV-C/TiO₂ derived by Ti₃C₂ calcined at different temperatures under full spectrum light illuminations, inset: the equivalent circuit.

The adsorption of N₂ on OV-C/TiO₂-600 was next observed by ESR spectra in Ar and N₂ atmosphere, respectively. As observed in Figure S1, the signal of oxygen vacancies in N₂ atmosphere is much weaker than that in Ar, which attributed to the efficient adsorption of N₂ on oxygen vacancies. Actually, our previous study has also demonstrated that oxygen vacancy is an efficient chemisorption and activation point of N₂ molecular by DFT calculation, with larger combination energy release, longer N≡N bond and shorter N-Ti distances than clean TiO₂ surface. In view of that the chemisorption is an essential step during the photocatalytic N₂
reduction processes, N$_2$-temperature-programmed desorption (N$_2$-TPD) was further performed to peruse the adsorption-desorption activation of N$_2$ on the surface of the prepared OV-C/TiO$_2$.

Referencing the previous report, the chemisorption of N$_2$ usually occurs at about 280 °C (on carbon) and 360 °C (on TiO$_2$), while the physical adsorption of N$_2$ occurs at about 120 °C. As displayed in Figure 7, the remarkable higher TCD signal of OV-C/TiO$_2$ than that of the commercial anatase TiO$_2$ shows the much better chemisoption of N$_2$ on the surface of OV-C/TiO$_2$ than that of the commercial anatase, which is crucial for the N$_2$ activation.

![Figure 7 N$_2$-TPD profiles of the commercial anatase TiO$_2$ and OV-C/TiO$_2$-600.](image)

Following with the adsorption of N$_2$ (step ①), there are 6 steps of hydrogenation and 2 steps of NH$_3$ desorption, as described in Figure 8. In this work, we further calculate the free energy and bond changes of N-N & N-Ti of every step, to describe the reaction pathways of N$_2$ conversion to NH$_3$ on the oxygen vacancy on TiO$_2$ surface. The optimized structures of selected N$_2$ reduction reaction intermediates are presented in Figure S15-23. As shown in Figure 8, N$_2$ on the oxygen vacancy on TiO$_2$ surface is reduced through an “alternating” pathway, being started from “distal” and finished by “enzymatic” pathways. The two N atoms in the N$_2$ molecules become asymmetric when it is adsorbed on the oxygen vacancy, resulting in the polarization of N≡N bond. Table S5 lists the bond distance changes of N-N and N-Ti with the hydrogenation and NH$_3$ desorption steps, listing the activation process of N$_2$ conversion to NH$_3$ on the oxygen site on TiO$_2$ surface. Detailedly, the hydrogenation steps are exothermic processes (③): -0.68 eV; ④): -0.16 eV, ⑤): -0.13 eV and ⑥):
1. $-2.66$ eV) except step ② to form $^*\text{N=NH}$ from $^*\text{N}_2$ (+0.06 eV) and step ⑧ to form $^*\text{NH}_2$ from $^*\text{NH}_3$ (+0.37 eV), while the NH₃ desorption steps are endothermic processes (⑦: +0.06 eV and ⑨: +0.69 eV). Based on these results, the reaction of N₂ in the oxygen vacancy on TiO₂ surface reduction to NH₃ is dominated by a Gibbs free energy releasing process, and the potential determining step (PDS) is ascertained to be the last step involved in the second NH₃ desorption, which is consist with the experimental results that the generated NH₃ can absolutely desorb into the solution only after reacting with 0.1M HCl regent. Our DFT calculations demonstrated that oxygen vacancy can effectively polarize N≡N bond and reduce it through a Gibbs free energy release leading alternating pathway with the second NH₃ desorption as the PDS.

**Figure 8** Minimum energy path for the N₂ conversion into NH₃ in the site of oxygen on the surface of TiO₂.

Overall, based on the studies and discussions above, a schematic illustration of photocatalytic N₂ fixation over OV-C/TiO₂ with oxygen vacancies is displayed in Scheme 2. With the doping of oxygen vacancy and carbon in the crystal of TiO₂, defect energy levels were introduced in the middle of forbidden zone, forming heteroatom energy band above the valence band⁸¹ and vacancy energy band¹² under the conduction band. The specific band structure of OV-TiO₂-600 was obtained by the Tauc-plot curve (Figure S24) and Mott-schokkty plots (Figure S25). Upon the irradiation of full spectrum light, electrons on the valence band of TiO₂ are excited and populated into the conduction band or vacancy states. Then the excited electrons on both the conduction band and defect states react with N₂ adsorbed on oxygen vacancies, producing NH₃ molecular. Meanwhile, the holes will react with CH₃OH. Several reasons can explain the enhanced N₂ fixation activity. Firstly, oxygen vacancies and doping carbon can broaden the range of the light absorbance, which helps to provide more electron-hole pairs and promote their separations;
secondly, oxygen vacancies capture the electrons on the conduction band, resulting in a prolonged lifetime of photocarriers; thirdly, oxygen vacancies act as adsorption and activation sites for N₂, enhancing and increasing the N₂ conversion to NH₃ through a Gibbs free energy decrease leading alternating pathway with a low energy barriers.

![Scheme 2 Diagram of the photocatalytic N₂ fixation mechanism over OV-C/TiO₂.](image)

4. Summary

In summary, OV-C/TiO₂ with the abundance of oxygen vacancies were successfully prepared by calcining Ti₃C₂ MXene at different temperatures. Notably, this strategy can control the amount of oxygen vacancy through a facial and reproducible process. All the prepared OV-C/TiO₂ catalysts show excellent photocatalytic N₂ fixation performance, which achieved the highest of 84 μmol g⁻¹ h⁻¹ at OV-C/TiO₂ with CH₃OH as the proton source, much higher than P25 and commercial A-TiO₂. The introductions of oxygen vacancies and carbon doping are the most crucial factor for such significant photocatalytic N₂ fixation performance, which not only enhance the generation of electron-hole pairs, reduce the recombination of electron-hole pairs, but also prolong the lifetime of photocarriers and enhance the chemisorption & activation of N₂ molecular. Most importantly, oxygen vacancies play efficient N₂ absorption site and active the N₂ atoms through a Gibbs free energy releasing leading pathway. The efficiency of photocatalytic N₂ fixation by TiO₂ is thus lifted to a high level, although it is still too low to realize the practical applications.

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References


45. Y. Liao, J. Qian, G. Xie, Q. Han, W. Dang, S. Wang, L. Lv, S. Zhao, L. Luo, W. Zhang, H.-Y.


